Tetrahedron Letters,Vol.30,No.30,pp 4007-4008,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Maxwell Pergamon Macmillan plc

PHOTOSENSITIZED ELECTRON TRANSFER OXIDATION OF 2-SUBSTITUTED 1,3-DITHIOLANE TO 1,3-DITHIOLANE-1-OXIDE[1]

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Abstract: Irradiation of a solution of 1,3-dithiolane, 1-cyanonaphthalene in O_2-saturated $CH_3CN:H_2O$ (3:1) at 350 nm furnishes good yields of 1,3-dithiolane-1-oxide.

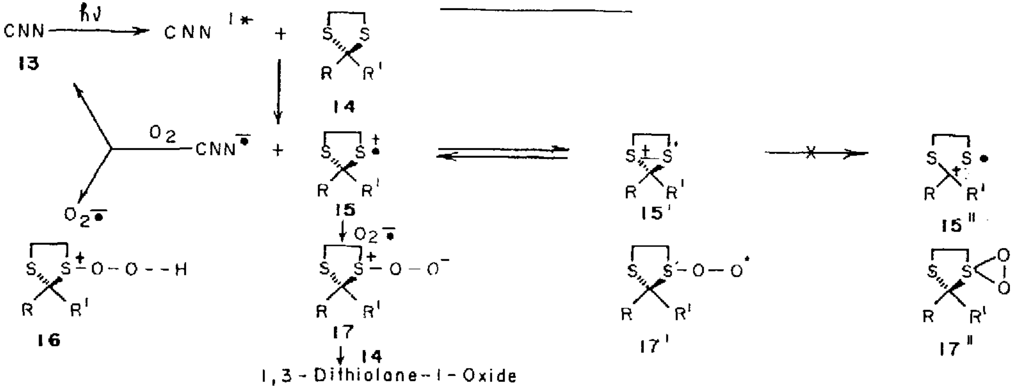
1,3-Dithiolanes constitute an important functional group in organic chemistry. However, its photochemistry remains underexplored. Eaton et al.[2] observed that the photolysis of 1,3-dithiolanes, in the absence of oxygen, led to product(s) by initial C-S bond cleavage, whereas Takahasi et al.[3] reported a unique photo-dethioketalization of various 1,3-dithiolanes in the presence of triplet sensitizers and molecular oxygen. Foote et al.[4] in a series of publications, have delineated the mechanistic details of the interaction between dialkyl sulfide and singlet oxygen, in which sulfides have been invoked invariably as a nucleophile. However, there are not enough examples where sulfide radical cations have been implicated in the photosensitized oxidation processes.[5,6] Fascinated by the nature of species involved, eg. distonic dithiolane radical cations[7] and superoxide, in such studies, the photochemistry of some of the 1,3-dithiolanes was studied under electron transfer conditions and the present letter describes a useful methodology for the preparation of 1,3-dithiolane-1-oxide.

SCHEME-1

1, n = 2
2, n = 3
3, n = 2 (80 %)
4, n = 3 (75 %)
5, R = H
6, R = CH_3
7, R = C_2H_5
8, R = C_6H_5
9, R = H (78 %)
10, R = CH_3 (72 %, 9:1)
11, R = C_2H_5 (75 %, 3:1)
12, R = C_6H_5 (60 %)

The photosensitized electron transfer oxidation was accomplished by irradiating (Rayonet Photoreactor, 350 nm) a solution of 1,3-dithiolanes (0.001 mole) with 1-cyanonaphthalene (CNN, 5×10^{-4} mole) in an oxygen saturated mixture of $CH_3CN:H_2O$ (3:1) in a pyrex vessel for 8-10 hrs. Oxygen bubbling was repeated intermittently during photolysis. Progress of reaction was monitored by GLC. Normally 90% of dithiolanes was consumed and after a usual work up, ie. removing CH_3CN on rotavapour, extracting organic compound in CH_2Cl_2 and purifying S-oxide by column chromatography, a satisfactory yield (60-80%) of 1,3-dithiolane-1-oxide was obtained (Scheme-1).[8] Although many variations in experimental conditions are possible as far as time of irradiation, degree of O_2-saturation, solvent composition and concentration of substrate and photosensitizer are concerned, above reaction conditions furnished satisfactory yields. The generality of this reaction is demonstrated in Scheme-1.[10] Normally only S-oxides were formed and there was no trace of sulfone or di-S-oxides.[8] The stereoselectivity of oxygenation was governed by steric factors. Thus, the major product of **10** & **11** contained oxygen syn to alkyl group, which could be easily ascertained by ^{1}H-nmr.

SCHEME-2



The tentative mechanism for this complex oxygenation process could be visualized as shown in Scheme-2, which is self explanatory as per the norms of SET-mechanism.[11,12] There is precedent for distonic radical cations **15'** and **15''**[7,13] and peroxysulfoxide **17**, diradical **17'** and cyclic peroxide **17''** formation.[4] Whereas **15'** might be responsible for the formation of only mono S-oxide, no products are isolated related to **15''**. In support of the above mechanism, it has been shown with **1** that CNN,H_2O and O_2-bubbling is a must for the success of reaction. Without anyone or without all of them, there is no change in the starting material under identical photolytic conditions. 1,3-Dithiolanes, as such, do not react with superoxide, even under exhaustive conditions.[14] Thus, radical cations are needed for this reaction. Mention must be made here that intermediates such as **17** could be obtained by reacting dithiolanes with singlet oxygen,[4] and that has indeed been the case. Thus, the reaction of **1** with $^{1}O_2$ gave **3** (10%).[14] The proposed mechanism also explains the need for polar protic solvent (H_2O) for stabilization of peroxysulfoxide **17** as **16**. 1,3-Dithiolane-1-oxide constitutes an important synthetic intermediate and the present photochemical methodology in a neutral and near aqueous medium should complement existing methods.

Acknowledgement: S.Y.B. and U.R.K. thank CSIR (India) for fellowship.

REFERENCES AND NOTES

1. NCL Communication No. 4672. **2.** R. Arad-Yellin and D.F. Eaton, J.Am.Chem.Soc., 1982, **104**, 6147. **3.** T.T. Takahasi, C.Y. Nakamura and J.Y. Satoh, J.C.S. Chem. Commun., 1977, 680. **4.** J.J. Liang, C.L. Gu, M.L. Kacher and C.S. Foote, J.Am.Chem.Soc., 1983, **105**, 4717 and references cited therein. **5.** M.A. Fox, P.K. Miller and M.D. Reiner, J.Org.Chem., 1979, **44**, 1103. **6.** T. Tezuka, H. Miyazaki and H. Suzuki, Tetrahedron Lett., 1978, 1959. **7.** "Organic Sulfur Chemistry", Ed. F. Bernardi, I.G. Csizmadia and A. Mangini, Elsevier, Oxford, 1985, p.485-500. **8.** Comparatively in mCPBA procedure,[2] more than 50% of dithiolane **1** remains unreacted and under exhaustive conditions i.e. warming up and longer time period, side products are formed. **9.** C.H. Chen and B.A. Donatelli, J.Org.Chem., 1976, **41**, 3053. **10.** All the new compounds eg. **11** and **12** gave satisfactory IR, ^{1}H-NMR and mass spectra. The known S-oxides were characterized by comparing the ^{1}H-NMR, IR, GC, TLC of authentic samples. **11.** P.S. Mariano in "Synthetic Organic Photochemistry", Ed. W.M. Horspool, Plenum Press, London, 1984, p.145-257. **12.** S. Futamura and Y. Kamiya, J.C.S. Chem. Commun., 1988, 1053. **13.** C.W. Byers, H. Gruen, H.G. Giles, H.N. Schott and J.A. Kampmeir, J. Am. Chem. Soc., 1972, **94**, 1016. **14.** S.Y. Bal and B. Pandey, unpublished results.

(Received in UK 12 April 1989)